



DEL/ZA04/00007

# Sertifikaat

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR  
DEPARTEMENT VAN HANDEL  
EN NYWERHEID

# Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE  
DEPARTMENT OF TRADE AND  
INDUSTRY

Hiermee word gesertifiseer dat  
This is to certify that

REC'D 05 JUL 2004

WIPO

PCT

the documents annexed hereto are true copies of:

Application forms P.1, P2 and provisional specification of South African Patent Application No. 2003/0585 as originally filed in the Republic of South Africa on 22 January 2003 in the name of SASOL TECHNOLOGY (PTY) LTD for invention entitled: "ESTERIFICATION CATALYST AND PROCESS FOR THE ESTERIFICATION OF ACIDS IN A HYDROCARBONS CONTAINING FEED."

Geteken te  
Signed at **PRETORIA**

in die Republiek van Suid-Afrika, hierdie  
in the Republic of South Africa, this

18<sup>th</sup> dag van  
day of May 2004

1 Registrar of Patents

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
**APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT**  
[Section 30 (1) - Regulation 22]

Revenue stamps or revenue franking machine  
impression

Official date stamp

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

21 01 **2003/0585**

(i) APPLICANT'S OR AGENT'S REFERENCE

**F433**

(ii) FULL NAME(S) OF APPLICANT(S)

71 **SASOL TECHNOLOGY (PTY) LTD**

(iii) ADDRESS(ES) OF APPLICANT(S)

**1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA**

TITLE OF INVENTION

(iv) 54 **ESTERIFICATION CATALYST AND PROCESS FOR THE ESTERIFICATION OF ACIDS IN A HYDROCARBONS CONTAINING FEED**

(v) The applicant claims priority as set out on the accompanying form P2.

The earliest priority claimed is Country: Number: Date:

(vi) This application is for a patent of addition to Patent Application No.

21 01

(vii) This application is a fresh application in terms of section 37 and is based on Patent Application No.

21 01

This application is accompanied by:

- (viii) ☒ 1. A single copy of a provisional specification of **11** pages.
- ☐ 2. Drawings of  sheets
- ☐ 3. Publication particulars and abstract (form P8 in duplicate).
- ☐ 4. A copy of Figure  of the drawings for the abstract.
- ☐ 5. An assignment of invention.
- ☐ 6. Certified priority document(s) (state number):
- ☐ 7. Translation of the priority document(s).
- ☐ 8. An assignment of priority rights.
- ☐ 9. A copy of the form P2 and the specification of SA Patent Application No.
- ☐ 10. A declaration and power of attorney form P3.
- ☐ 11. Request for ante-dating on form P4.
- ☐ 12. Request for classification on form P9.
- ☐ 13. In terms of section 31(1) the applicant has added additional revenue stamps to this form for claiming priority after 12 months but before 15 months from the priority filing date.
- ☒ 14. Form P2 + copy

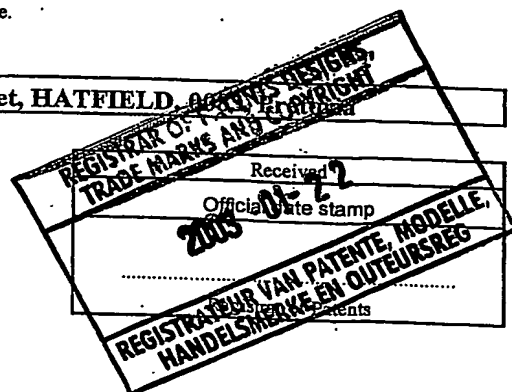
21 01

(ix) 74 Address for service: **HAHN & HAHN INC, 222 Richard Street, HATFIELD.**

Dated this **22** day of **January** 20 **03**

Signature of applicant(s) or agent

This duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with an official stamp



REPUBLIC OF SOUTH AFRICA

FORM P2  
PATENTS ACT, 1978

## REGISTER OF PATENTS

OFFICIAL APPLICATION NO.		LODGING DATE: PROVISIONAL		ACCEPTANCE DATE	
21 2003/0585		22 22 Jan 2003		47	
INTERNATIONAL CLASSIFICATION		LODGING DATE: COMPLETE		GRANTED DATE	
51		23			
INTERNATIONAL APPLICATION NO.		LODGING DATE: INTERNATIONAL			
FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)					
71 SASOL TECHNOLOGY (PTY) LTD					
APPLICANTS SUBSTITUTED:				DATE REGISTERED	
71					
ASSIGNEE(S)				DATE REGISTERED	
71					
FULL NAME(S) OF INVENTOR(S)					
72 BOLDER, Franciscus, Hermanus, Antonius					
PRIORITY CLAIMED		COUNTRY	NUMBER	DATE	
NB - Use International abbreviation for country (See Schedule 4)		33	31	32	
TITLE OF INVENTION					
54		ESTERIFICATION CATALYST AND PROCESS FOR THE ESTERIFICATION OF ACIDS IN A HYDROCARBONS CONTAINING FEED			
ADDRESS OF APPLICANT(S)/PATENTEE(S)					
1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA					
ADDRESS FOR SERVICE			REF		
74 HAHN & HAHN INC, PRETORIA			F433		
PATENT OF ADDITION NO.		DATE OF ANY CHANGE			
61					
FRESH APPLICATION BASED ON		DATE OF ANY CHANGE			

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
**PROVISIONAL SPECIFICATION**  
[Section 30(1) - Regulation 27]

OFFICIAL APPLICATION NO

21 01 **2003/0585**

LODGING DATE

22 **22 Jan 2003**

FULL NAME(S) OF APPLICANT(S)

71

**SASOL TECHNOLOGY (PTY) LTD**

FULL NAME(S) OF INVENTOR(S)

72

**BOLDER, Franciscus, Hermanus, Antonius**

TITLE OF INVENTION

54

**ESTERIFICATION CATALYST AND PROCESS FOR THE ESTERIFICATION OF  
ACIDS IN A HYDROCARBONS CONTAINING FEED**

## ESTERIFICATION CATALYST AND PROCESS FOR THE ESTERIFICATION OF ACIDS IN A HYDROCARBONS CONTAINING FEED

### Field of the Invention

The invention provides an esterification catalyst and an esterification process for the esterification of acids in a hydrocarbons containing feed stream.

### Background to the Invention

Fischer-Tropsch (FT) product streams are known to contain organic acids, carbonyls, alcohols and other oxygenates, but no sulphur compounds. Removing acids from FT products would allow these products to be hydrogenated at lower temperatures over nickel or other catalyst without introducing sulphur to the process. It would also reduce corrosion which is a general problem.

### Summary of the Invention

According to a first aspect of the invention, there is provided an esterification catalyst including one or more catalytically active metal oxides, wherein one of said catalytically active oxides is molybdenum oxide.

The molybdenum of the catalyst may be supported on an alumina substrate.

The catalyst may be activated by reduction in a hydrogen rich atmosphere at a temperature exceeding 200°C.

The catalyst may be activated by reduction in a hydrogen rich atmosphere at a temperature of about 250°C at atmospheric pressure.

The catalyst may be activated by reduction in a hydrogen rich atmosphere at a temperature of about 470°C at atmospheric pressure.

5 According to a second aspect of the invention there is provided an esterification process for the reduction of acids in a hydrocarbon containing composition, said process including contacting the hydrocarbon containing composition with an esterification catalyst at esterification temperature and pressure.

10 The esterification catalyst may be a molybdenum oxide on alumina catalyst as described above.

The esterification temperature may be from 100°C to 320°C.

15 The esterification temperature may be from 170°C to 250°C.

Typically the esterification temperature is from 190°C to 210°C.

The esterification pressure may be from atmospheric pressure to 100 Bar, typically from 1 to 55 Bar.

20 The hydrocarbon containing composition may include hydrocarbons of less than 24 carbons i.e. lower than C<sub>24</sub>.

25 The hydrocarbon containing composition may be a C<sub>4</sub> to C<sub>20</sub> hydrocarbons containing composition.

The hydrocarbon containing composition may be a Fischer-Tropsch (FT) condensate fraction.

By FT condensate fraction is meant a condensate fraction of the Fischer-Tropsch reaction products. The condensate fraction is typically obtained as the light stream or overhead stream from a separator after a Fischer-Tropsch reactor in which the Fischer-tropsch reaction has taken place. Table A below provides typical data for the FT condensate stream.

**Table A: Typical Fischer-Tropsch product after separation into two fractions**  
(vol% distilled)

	FT Condensate (< 270°C fraction)	FT Wax (> 270°C fraction)
C <sub>5</sub> -160°C	44	3
160-270°C	43	4
270-370°C	13	25
370-500°C		40
> 500°C		28

The hydrocarbon containing composition may have an initial acid level of 0.5 mg KOH/g or higher.

Typically, the initial acid level in the hydrocarbon containing composition may be as high as 12 mg KOH/g.

The alcohol to acid ratio in the FT hydrocarbon may be between 14 and 92 on a molar basis.

Methanol or another alcohol may be added to the FT hydrocarbon feed to increase the alcohol to acid ratio.

The product of the process may have an acid level of less than or equal to 0.5 mg KOH/g, generally from 0.1 mg KOH/g to 0.3 mg KOH/g.

- 5 The process may be carried out in a trickle bed reactor.

The process may be carried out at an LHSV of from 0.5 and 2 h<sup>-1</sup>.

### Examples of Performing the Invention

10

The examples that follow are not intended to limit the scope of the invention and are by way of illustration of the invention only.

### Catalyst and operating procedures

15

A commercial molybdenum on alumina catalyst from BASF (M8-30) was used for the experiments. The catalyst is produced in 5 mm diameter extrudates. The extrudates were crushed and sieved between 0,5 and 2,83 mm and diluted 1:1 with carborundum (0,5-2mm).

20

Table 1 catalyst composition

**Mo/Al<sub>2</sub>O<sub>3</sub> catalyst**

**(BASF M8-30)**

component	Na <sub>2</sub> O	MoO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	water	total
Mass %	0.07	15.61	83.87	0.46	100.00

- 25 The catalyst was dried in situ in a hydrogen flow at 125°C and pretreated by reduction with hydrogen either at 470°C for 10 hours or at 250°C for 5 hours . The temperature programmed reduction (TPR) shows a reaction with hydrogen around 430°C.



The experiments were carried in a 27,5 mm ID bench scale reactor with a total length of 1,5 meter. Bed temperatures were measured with 6 thermocouples axially spaced inside a 6mm OD thermocouple sheath. The reactor was operated in the down flow mode, at 55 bar, 1 l/(lcat.h) liquid hourly space velocity (LHSV) and between 385 and 500 l<sub>n</sub>/(lcat.h) hydrogen GHSV.

### Molybdenum oxidation state

The reduction in a flow of hydrogen was investigated using TPR, which showed one peak at around 430°C and another one above 800°C. The sample was dried in an oven at 250°C prior to the reduction to remove adsorbed water. The percentage molybdenum and aluminium was determined after drying. The mass percentages of the metal oxides did not add up to 100% and it was assumed that the balance was water. From this value the percentage molybdenum oxide in a water free sample was calculated. The hydrogen uptake per gram of water-free catalyst was calculated from the area under the first peak. This amount was in reasonable agreement with a reduction to Mo<sup>5+</sup> as shown in table 2 below.

Table 2 reduction in H<sub>2</sub> (TPR)

reduction	MoO <sub>3</sub> -----> MoO <sub>2</sub>	MoO <sub>3</sub> -----> Mo <sub>2</sub> O <sub>5</sub>
mass loss/g cat	0.0172	0.0086
mol O/g cat	0.0011	0.0005
H <sub>2</sub> needed (l/g cat)	0.0241	0.0120
actual H <sub>2</sub> consumption	0.0093 l/g cat	

The crystallite size was too small for an XRD analyses to confirm the Mo oxidation state.

## Examples

### Example 1

The feed in the first experiment consisted of a C<sub>4</sub>-C<sub>20</sub> Fischer Tropsch product cut. The hydrocarbon product was passes through a caustic wash which reduced the acids to about 0,5 mg KOH/g. The molar ratio of alcohols to acids in the hydrocarbon feed was 92.

The catalyst was pretreated in hydrogen at 470°C.

The results are shown in table 3 below

Table 3

catalyst 1: treated at 470°C					
T	°C	250	210	190	210
LHSV	h-1	1.5	1.5	1.5	1.5
<b>feed</b>					
ratio alcohol/acid		92	92	92	16.5
acid	mgKOH/g	0.38	0.38	0.38	2.33
carbonyl	mass% as MEK	0.32	0.32	0.32	0.11
alcohol	mass% as C7	6.96	6.96	6.96	7.74
ester	mgKOH/g	0.82	0.82	0.82	0.68
olefins	g Br/100g	47.8	na	47.8	42.9
<b>product</b>					
acid	mgKOH/g	0.01	0.01	0.01	0.02
carbonyl	mass% as MEK	0	0.022	0.09	0.18
alcohol	mass% as C7	0	0.64	6.47	6
ester	mgKOH/g	0	1.2	1.53	2.97
olefins	g Br/100g	80.8	na	45.8	40.8
<b>conversion</b>					
acid+ ester	(mol/kg)	0.021	0.000	-0.006	0.000
acids conversion	%	97.37	97.37	97.37	99.14

At 250°C the various oxygenates were nearly completely removed. The residual acids in the effluent stream was 0,01 mg KOH/g. The concentration of olefins doubled, from 40 to 80 gBr/100g.

- 5 In the same experiment, in the temperature range of 190 to 210°C, the acids still reacted nearly completely to esters but less of the other oxygenates reacted. . The products of these reactions were not identified

The olefinity of the effluent was similar to the value of the feed..

10

### Example 2

- 15 In this example the feed consisted of C<sub>4</sub> to C<sub>20</sub> paraffin with a higher acid level (2,3 mg KOH/g). The alcohol concentration was the same as in the previous feed, about 7 mass% as C<sub>7</sub> alcohol. The molar ratio of alcohol to acid of this feed was 16,5.

The catalyst treatment was the same as in example 1.

- 20 The results are shown in table 3 above.

- 25 The residual acids in the effluent were between 0,02 and 0,03 mgKOH/g at 210°C. When the temperature was increased to 250°C (after about 5 days), the residual acid level increased to 0.15 mg KOH/g. This may be ascribed to a decrease of the alcohol concentration due to secondary reactions. As a result the alcohol to acid ratio decreased causing a decrease in the conversion to esters.

### Example 3

- 30 In this experiment the catalyst was pretreated in hydrogen at 250°C.

The feed for this experiment was a light condensate fraction derived from low-temperature Fischer-Tropsch synthesis (mainly in the naphta and diesel range with a small fraction waxy material suspended in it). The acids varied between 1,9 and 2,5 mg KOH/g.

5

The results are shown in table 4 below

10

At a temperature of 210°C, 1 h<sup>-1</sup> LHSV and an alcohol to acid ratio of 14 the conversion of the acids was 98.8 % resulting in an acid number of 0.03 mg KOH/g in the effluent. The same results were obtained at 1,5 h<sup>-1</sup> LHSV, which indicated that the reaction was close to equilibrium.

15

The stability of the catalyst was tested at 220°C for 13 days at 1 h<sup>-1</sup> LHSV with a different feed (alcohol to acid ratio of 19). The residual acids were 0.05 mgKOH/g and remained stable for as long as these conditions were maintained.

At temperatures between 250 and 290°C the acid content of the product increased and only at 310°C did they decrease. Significantly, the olefinitiy of the product did not increase at these temperatures.

Table 4

catalyst 2: treated at 250°C								
T	°C	210	210	220	230	250	290	310
LHSV	h-1	1	1.5	1	1	1.5	1.5	1.5
<b>feed</b>								
ratio alcohol/acid		14	14	19	19	14	14	14
acid	mgKOH/g	2.5	2.5	1.9	1.9	2.5	2.5	2.5
carbonyl	mass% as MEK	0.46	0.46	0.4	0.4	0.46	0.46	0.46
alcohol	mass% as C7	7	7	7.4	7.4	7	7	7
ester	mgKOH/g	0.75	0.75	0.97	0.97	0.75	0.75	0.75
olefins	g Br/100g	66.6	66.6	68.3	68.3	66.6	66.6	66.6
<b>product</b>								
acid	mgKOH/g	0.03	0.03	0.05	0.09	0.19	0.6	0.03
carbonyl	mass% as MEK	0.26	0.31	0.21	0.21	0.24	0.29	0.08
alcohol	mass% as C7	6.3	7.2	3.6	3.4	3	0.68	0.18
ester	mgKOH/g	3.2	3.4	2.6	2.6	3.3	0.59	0.05
olefins	g Br/100g	65.0	65.0	71.2	63.2	64.2	67.7	66.0
<b>conversion</b>								
acid+ ester	(mol/kg)	0.000	-0.003	0.004	0.003	-0.004	0.037	0.056
acids conversion	%	98.80	98.80	97.37	95.26	92.40	76.00	98.80

5 Carbonyls were only partly removed and the temperature made little difference to the conversion.

Carbonaceous material was again deposited on the catalyst during the run. The carbon content was not determined this time.

10 Depending on the temperature, alcohols and carbonyls may react to form a range of compounds and a change in the alcohol to acid ratio will shift the equilibrium from ester to free acids.

Apart from esterification, alcohols can undergo a variety of other reactions:

- 15
- aldol condensation with aldehydes
  - acetal and ether formation
  - dehydration to olefins

There was insufficient evidence to determine whether the “dehydration to olefins” reaction took place because the olefin level did not increase consistently. Temperatures of well above 300°C are required to dehydrate significant amounts of ethanol and propanol to the corresponding olefins.

5

Fresh Mo/Al<sub>2</sub>O<sub>3</sub> catalyst showed initially considerable catalytic activity towards both esterification and dehydrogenation/dehydration reactions. In example 1, at the beginning of the run all oxygenates were removed at 250°C and the olefins concentration doubled. The latter reactions were however short lived.

10

The same trend was found in example 2: after 3 weeks on line the oxygenates could no longer be removed at a temperature of 250°C. The temperature had to be increased to 310°C before the bulk of the oxygenates was removed.

15

The esterification reaction was not affected by either the reduction temperature or the catalyst age or the run history. The data from all 3 examples fit the same graph as a function of temperature as shown in figure 1.

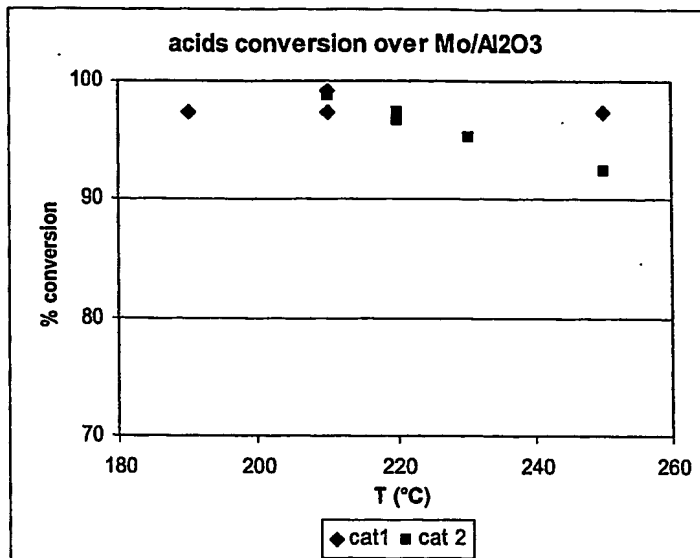
20

Other reactions were catalysed as well and these were dependant on the catalyst age and the run history. In example 1, at the early stage of the run, the olefinity of the product increased considerably at 250 °C. In example 2, after 3 weeks on line, the olefinity did not change when the temperature was increased to 250 °C..

003/0585

Esterification - Rev 5

Figure 1 Conversion of acids to esters over Mo/Al<sub>2</sub>O<sub>3</sub>



DATED THIS 22nd DAY OF JANUARY 2003

  
HAHN & HAHN  
AGENT FOR APPLICANT